C+S

PATENT SPECIFICATION (11) 1450446

1450446

(21) Application No. 56450/73 (22) Filed 5 Dec. 1973
(31) Convention Application No. 314532 (32) Filed 13 Dec. 1972 in
(33) United States of America (US)
(44) Complete Specification published 22 Sept. 1976
(51) INT CL² D06M 13/44 15/54 15/64//C08L 61/20
(52) Index at acceptance
D1P 21Y 235 23Y 240 24X 24Y 272 27Y 361 364 36Y 370 385 390 39Y 402 490 49Y 50Y 510 51Y 560 562 567 568 56Y 570 580 581 586 588 59X 59Y 610 612 621 622 62Y 632 634 649 65Y 660 662 66Y 70Y 74X 74Y 752 75Y 795 798 L4
C3R 38B1B 38B3C 38C 38D3A 38D7X 38N1X 38N4 C11 C12 C16 C8R L1A L1B L2X L4C L6H

(19)

(72) Inventor MARSHALL W. DUKE

(54) FIRE RETARDANT FABRICS AND METHOD FOR PREPARATION THEREOF

(71) We, UNITED MERCHANTS AND MANUFACTURERS, INC., a corporation organized and existing under the laws of the State of Delaware, United States of America, of 1407 Broadway, New York, New York 10018, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention pertains to the field of fire retardant textile fabrics. More particularly, this invention concerns a method of treatment of cellulose-containing fabrics to impart a fire-retardancy thereto.

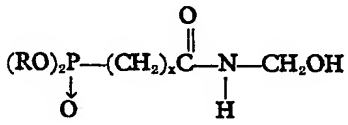
Numerous methods for treating cellulose containing fabrics to render such fabrics fire-retardant have been suggested. Generally, these methods reside in the impregnation of the fabric with a fire retardant chemical.

One of the best known fire retardant chemicals, particularly for use with cellulose derived textiles, has been tetrakis (hydroxymethyl) phosphonium chloride, commonly abreviated THPC. This chemical has been used in a variety of modes and procedures including one and two stage processes in conjunction with nitrogen containing compounds, such as, aminoplast resins. (See for example, U.S. Patents 3,421,923 and 3,556,840).

All of these type processes possess one or more disadvantages, such as for example, they produce undesirable fabric stiffness or poor hand, poor durability of the fire retardant finish after washing, and reduction in tensile strength and tear strength of the treated fabrics. Additionally, certain of the processes known heretofore result in undesirable chemical deposits on the fabrics.

We have discovered a new method for rendering a cellulose textile fabric fire retardant whereby the resulting fabric possesses not only durable fire-retardancy, but also a soft hand and tensile properties similar to those of the untreated fabric.

The present process is carried out by impregnating the fibres of a cellulose-containing fabric with an aqueous mixture of an aminoplast precondensate, an acid having a first hydrogen dissociation constant in the range from 2×10^{-1} to 5×10^{-5} and a dialkyl phosphono-methylol alkylamide having the formula



(I)

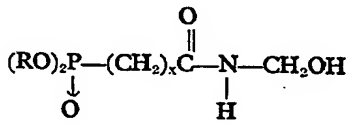
wherein R is lower alkyl having 1 to 6 carbon atoms and x is an integer from 1 to 3, thereafter polymerizing the precondensate in the impregnated fabric while the fibers thereof are in a wet and swollen state, and then drying, curing, washing and drying the impregnated fabric.

The process of the present invention may be conveniently carried out commercially and avoids the disadvantages of prior art processes as described hereinabove. Particularly, we have found that with the present process, decreased levels of the dialkyl phosphono methylol alkylamide can be used to achieve satisfactory levels of fire retardancy.

The present process can be used for treating all types of cellulose-containing fabrics (including those which are cellulose-derived), such as those made from cotton fibers, regenerated cellulose, jute, manila, hemp, sisal, and ramie or blends of such materials with synthetic fibers especially where the fabric has a cellulose content of at least 80 percent by weight. The process is especially useful

for the treatment of cotton fabrics for clothing materials, tents and awning materials. Generally, the process of the present invention and the products obtained therefrom are advantageous in those cases, where cellulose-containing materials are exposed to the danger of fire and wherein, in addition, to high flame resistance, high mechanical strength after repeated washing is required.

In accordance with the present invention, the fabric is first impregnated with an aqueous mixture of an aminoplast precondensate, an acid having a first hydrogen dissociation constant in the range from 2×10^{-1} to 5×10^{-5} and a dialkyl phosphono-methylol alkylamide having the formula



(I)

wherein R is lower alkyl having 1 to 6 carbon atoms and x is an integer from 1 to 3.

Such an impregnation can be carried out by methods well known to the art such as dipping or padding, with padding being preferred. Preferably, the amount of aminoplast applied to the fabric is in the range from 2 to 25 percent, and most preferably from 5 to 10 percent by weight based upon the weight of the fabric.

Water soluble, hardenable aminoplasts suitable for use in the present process primarily include hardenable aminotriazine resins that are soluble in water or possess limited solubility in water and which may be etherified. Such aminoplasts are obtained by methods well known in the art such as the condensation of formaldehyde with melamine, acetoguanamine, benzoguanamine, of formoguanamine. Mixtures of such condensation products are also suitable. Particularly preferred condensation products are those of 2—3 moles of formaldehyde with one mole of melamine.

Those condensation products of limited water-solubility are colloidal intermediate products which are first produced on further condensation beyond the crystalline methylol stage. They are characterized in that they are precipitated from the concentrated aqueous solution by the addition of water (See Kolloid-Zeitschrift, Vol. LVII, October-December 1931, page 233).

The completely water-soluble condensation products may be applied in the form of aqueous solutions. The condensation products of limited solubility may be used either in the form of solutions of the solubilized condensation products, i.e., those made soluble with acids, or in the form of emulsions.

Suitable acids for use in the present invention include phosphoric acid, and acids of substantially equivalent strength as phosphoric, e.g., oxalic, phthalic, chloroacetic, cyanoacetic, malonic, and tartaric acids which are slightly weaker than phosphoric acid, e.g., formic and acetic; and acids slightly stronger than phosphoric acid, e.g., benzene sulfonic acid.

Preferably, the amount of acid used is in the range from 0.5 to 5, and preferably from 1 to 3 weight percent based on the weight of the fabric. As noted, the third component of the mixture is a compound having the general formula designated by I. Particularly preferred are those compounds having the general formula I wherein R is methyl or ethyl and x is 2.

Preferably, the amount of compound I used is in the range from 15 to 30 weight percent and preferably in the range from 18 to 26 weight percent based on the weight of the fabric. In any event, sufficient amount of compound I is usually applied to the fabric to produce a final phosphorus content in the resulting fabric of from 1 to 5 percent and, preferably, from 1.4 to 2.5 percent based on the total weight of the fabric.

In addition, the solution may also contain urea as well as other nitrogenous compounds capable of reacting with the hydroxy methyl-(methylol) group. These may be in quantities from 1 to 10 weight percent and, preferably, from 1 to 3 weight percent of the solution. Typical examples of materials are ethylene urea, propylene urea, guanidine dicyandiamide, oxamide, thiourea and polyethyleneimines.

Following the impregnation step, the aminoplast precondensate is polymerized while the fibers are maintained in a wet and swollen state. Such a process is generally termed "wet fixing". This polymerization may be carried out under steam and/or under pressure.

The usual process used for the polymerization is to first remove any excess of the impregnation solution from the fabric as by squeezing or centrifugation. The fabric is then stored in a closed chamber such that the fabric remains wet for the entire period of storage. The storage time depends on the temperature of storage. Thus, for example, the storage may be carried out for one minute if steam is used to control temperature, i.e., direct application of steam to the fabric; for 15 minutes if the storage temperature is 85°; and for 20—24 hours if the temperature is room temperature. It is critical, however, that the fabric not be allowed to dry during the storage period. Thus, it may also be necessary to control the humidity of the storage chamber.

Specific methods for such wet fixing are well known in the art (see for example *Textile Research Journal*, pages 44—64,

January, 1971; Bullock, J. B. and Welch, C. M. Textile Research Journal 35 pages 459, 471, 1965; and U.S. Patents 3,434,875 and U.S. Patent No. 3,546,006.

After the wet fixing step, the fabric is dried, usually by air drying at temperatures up to about 400°F, and preferably in the range from 240—290°F.

After drying, the fabric is subjected to a curing step. Generally, the fabric is cured at a temperature ranging from 300 to 400°F for a period of time from 2 to 20 minutes. Typically, in plan practice, a 4 to 8 minute cure at about 320°F would be used.

A major advantage of the present invention is evident in the curing step. Thus, with this present invention, a "hard" cure can be used without suffering appreciable loss of softness, tensile strength, or fabric whiteness. Contrary to most aminoplast resin systems, this invention allows a second curing without appreciable damage, if indicated, to increase phosphorus fixation for better fire retardancy.

The fabric may also be subjected to a peroxidation step prior to washing in order to eliminate any possible odor when the fabric is wet and to avoid losses in fire-retardancy when the fabric is exposed to sunlight. The peroxidation step involves treatment with an oxidant, such as, for example, hydrogen peroxide or sodium perborate. The peroxidation may be carried out at elevated temperatures in a continuous process such as in an "open soaper" or batchwise in a dye beck. Alternatively, the oxidant may be padded onto the fabric while cold, followed by holding the fabric in a wet state for from 0.5 to 18 hours and then washing or rinsing the fabric. Such peroxidation methods are conventional in the art and the particular method used is not critical to the present invention.

A preferred back wash procedure utilizes a two-stage treatment. The first stage is a wash with alkali to neutralize any acidity and the second stage is an alkaline peroxidation to avoid residual odor in the fabric. In mill practice, an open soaper, jig or beck may be used to apply soda ash followed by a mixture of soda ash and sodium perborate. The fabric is then washed or rinsed and dried in the conventional manner.

The resulting fabric possesses a soft hand, durable fire retardancy and tensile properties similar to those of the fabric prior to treating. Such fabric is typically characterized by a phosphorus content in the range from about 1 to 5 percent by weight and a nitrogen content in the range from 1 to 6 percent by weight, all weights being based on the weight of the fabric.

The following examples illustrate our invention:

Fabric hand was determined by subjective evaluation of two or more qualified fabric examiners. Stiffness was determined by ASTM method D 1388-64. Tensile strength was measured by the Grab tensile method (ASTM D 1682-64). Fire retardancy was measured by Department of Commerce DOC, FF 3-71 or AATCC 34-1969.

Example 1

An 100% cotton flannelette is impregnated with an aqueous mixture of 10% by weight of a methylated trimethylolmelamine resin, 22% by weight of di-methyl phosphono methylol propionamide, 3% by weight of phosphoric acid and 1% by weight of urea. The fabric stretched to its finished fabric dimensions, rolled up and held wet 20 hours at room temperature. The fabric then dried. Any conventional drier, such as a tenter frame, loop drier or air-lay slack drier can be used. The dried fabric is cured at 310°F for 5 minutes, and back washed with sodium carbonate and a sodium carbonate/sodium perborate mixture in an open soaper. The fabric was then dried using steam heated cans. The resulting fabric was durably fire retardant and possessed a soft hand.

Example 2

An "80 square" cotton print cloth was impregnated with a solution of 26 percent by weight of di-ethyl phosphono methylol propionamide, 5% methylated trimethylolmelamine, 3% phosphoric acid, 1% urea, and 65% water by weight. The fabric was then handled as in Example 1 through the curing step. The backwashing was carried out in a jig instead of an open soaper and the final drying was on a tenter frame instead of steam heated cans. The fabric was durably fire retardant and possessed a soft hand.

Example 3

A pigmented printed cotton terry cloth was impregnated with a solution of 20% di-methyl phosphono methylol propionamide, 5% methylated trimethylolmelamine, 3% phosphoric acid, 1% urea and 71% water by weight. The fabric was the treated in accordance with the procedure set forth in Example 1. The resulting fabric possessed durable fire retardance and a soft hand.

Example 4

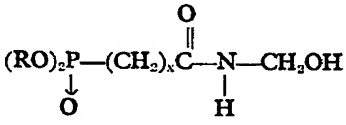
A fabric composed of a blend of 13 percent polyester and 87 percent cotton (fabric weight=5.5 ounces per square yard) was treated with the process of the present invention using two different impregnating solutions. Tthe first impregnating composition was composed of 25% di-methyl phosphono methylol propionamide, 5% trimethylolmelamine and 2.4% phosphoric acid, all percents being by weight based on solids. The second composition was composed of

30 weight percent dimethyl phosphono methylol propionamide, ten percent trimethylolmelamine, and 2.4% phosphoric acid.

The fabrics were impregnated with the impregnation solutions in the usual manner and then stored wet for twenty hours. Thereafter the samples were dried in the conventional mill equipment at 250—260°F. The fabrics were then cured for four minutes at 320°F and backwashed with soda ash, sodium perborate and a surfactant and then dried. The final fabrics in each case were fire retardant as measured by the vertical tests of the DOC FR3-71 Sleepwear Standard. Both samples possessed good fabric properties and hand.

WHAT WE CLAIM IS:—

1. A process for rendering a cellulose containing fabric fire retardant which comprises impregnating the fibres thereof with an aqueous mixture of an aminoplast precondensate, an acid having a first hydrogen acid dissociation constant in the range from 2×10^{-1} 5×10^{-5}, and a dialkyl phosphono-methylol alkylamide having the formula



(I)

wherein R is lower alkyl having 1 to 6 carbon atoms and x is an integer from 1 to 3, thereafter polymerizing the precondensate in the impregnated fabric while the fibers are in a wet and swollen state, and then drying, curing, washing and drying the impregnated fabric.

2. A process according to claim 1 wherein the fabric has a cellulose content of at least 80% by weight.

3. A process according to claim 1 or 2 wherein the fabric is impregnated with 2 to 25 percent aminoplast precondensate based upon the weight of the fabric.

4. A process according to claim 1, 2 or 3 wherein the fabric is impregnated with sufficient of said dialkyl phosphono-methylol alkylamide to produce a phosphorus content in the final fabric in the range from 1 to 5 percent by weight based on the total weight of the fabric.

5. A process according to any preceding claim wherein the amount of said acid is in the range from 0.5 to 5 percent by weight based on the weight of the fabric.

6. A process according to any preceding claim wherein the aqueous mixture contains:—

acid: 1 to 3 percent percent;
aminoplast resin: 5 to 10 weight percent;
dialkyl phosphono methylol amide: 18 to 26 weight percent,

all weights being based on the weight of the mixture.

7. A process according to any preceding claim wherein the aqueous mixture further contains urea, ethylene urea, propylene urea, guanidine, dicyandiamide, oxamide, thiourea, or polyethyleneimine.

8. A process according to claim 6 wherein the amount of the nitrogenous compound is in the range from 1 to 3 weight percent based on the weight of the mixture.

9. A process according to any preceding claim wherein subsequent to curing and prior to washing the fabric is subjected to peroxidation.

10. A process according to claim 9 wherein just prior to said peroxidation the fabric is subjected to an aqueous wash under alkaline conditions.

11. A process according to any preceding claim wherein R is methyl and x is 2.

12. A process for rendering cellulose containing fabric fire retardant substantially as described in any of the Examples herein.

13. A cellulose-containing fabric rendered fire retardant by a process according to any preceding claim.

REDDIE & GROSE,
Agents for the Applicants,
6, Bream's Buildings,
London, EC4A 1HN.

Reference has been directed in pursuance of section 9, subsection (1) of the Patents Act 1949, to patent No. 1,011,572.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1976.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.